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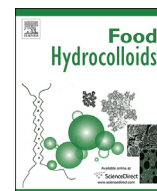
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The influence of co-solutes on tribology of agar fluid gels



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ABSTRACT

The effects of glucose and glycerol on the lubrication properties of agar fluid gels have been studied using soft tribology. A novel approach using the sediment and supernatant of centrifuged fluid gels has allowed investigation of the distinct contributions of both the gelled particulate phase and the continuous phase on fluid gel tribology. The friction coefficient of both the particulate phase and fluid gels was significantly lower than that of the continuous phase across the three lubrication regimes. This indicates that particle entrainment occurs at all entrainment speeds, enhancing lubrication by prevention of surface contact.

Softer fluid gel particles produced with intermediate levels of glycerol (up to 30%) show increased friction as would be expected for an increased contact area between the tribological surfaces. At high levels of glycerol, the friction does not increase. It is proposed that soft particles are produced but the increasing friction is overcome with the increased lubrication from the more highly viscous continuous phase. In contrast, the presence of intermediate levels of glucose (up to 30%) increases the friction of the aqueous continuous phase but does not affect the particle properties. Texture analysis, rheology and light scattering techniques were used to elucidate the structural changes of the fluid gels induced by the addition of co-solutes and the influence this has upon lubrication.

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1. Introduction

Fluid gels are concentrated suspensions of micro-gel particles dispersed in a continuous medium, typically water, and are produced by applying a shear field to the hydrocolloid solution while the sol–gel transition is taking place (Norton, Frith, & Ablett, 2006; Norton, Jarvis, & Foster, 1999). Application of fluid gels is of increasing interest to the food industry because of their ability to generate film thickness in the flow conditions that prevail during food processing in the mouth, potentially imparting desirable mouthfeel and texture attributes (e.g. smoothness) (Malone, Appelqvist, & Norton, 2003). The lubrication properties of fluid gels, which have been shown to be greatly influenced by the physical properties of particles (e.g. size, elasticity) (Gabriele, Spyropoulos, & Norton, 2010; Mills, Koay, & Norton, 2013), can be measured using tribology (thin-film rheology).

In this work, we used fluid gels produced from agar which is a seaweed hydrocolloid composed by mixtures of neutral agarose and charged agaropectin, in proportions that vary depending on both the production process and the raw material (Araki, 1956;

Phillips and Williams, 2009). Agarose is the polysaccharide with the gelling capability of agar and consists in alternating units of 3-linked β -D-galactopyranose and 4-linked 3, 6-anhydro- α -L-galactopyranose (Araki, 1956). The gelling temperature of agar varies depending on the degree of methoxylation of the agarose chain which is characteristic of the seaweed species from which the agar has been extracted (Armisen & Galatas, 2000).

As the gelling temperature of agar is approached, intra-molecular hydrogen bonds start to form between the agarose chains, followed by the formation of inter-molecular hydrogen bonds between the two distinct polysaccharide chains (Tako & Nakamura, 1988). The mechanism for gelation involves a coil to double helix transition and a subsequent aggregation of these helical domains to create a three dimensional structure (Arnott et al., 1974; Morris, 1986; Schafer & Stevens, 1995).

Upon cooling the agar solution under shear below the agar transition temperature, kinetic competition between the process of gel network formation and the shear induced break-up of the network occurs. The result of these two competing mechanisms determines the physical properties of the resulting fluid gel particles as well as the extent of inter-particle interactions. The control over the conformational ordering kinetics is achieved by the applied cooling rate such that a range of viscoelastic properties can be produced by manipulation of the processing conditions.

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The fluid gel formation is kinetically controlled by the number of available junction zones, where the rate of ordering is a function of polymer concentration, temperature and solvent quality. Thus, it is expected that changes in the degree of solvation of the hydrocolloid due to the presence of co-solutes will greatly affect the structure of the fluid gel particles and hence their lubricating properties. Although the effects of sugars and polyols on the material properties of quiescent agar gels have been widely reported in the literature, no published study has investigated the formation and lubrication properties of fluid gels mixed with such co-solutes.

The first objective of this work is to provide a comprehensive understanding of the mechanisms underlying the lubrication properties of agar fluid gels. The lubricating behaviour of agar fluid gel was investigated by [Gabriele et al. \(2010\)](#) who proposed a conceptual model for fluid gel lubrication. However, in order to rationalize these findings in terms of particle properties, it is required to decouple the relevant contributions of both the continuous phase and the particulate phase to fluid gel lubrication. To this end, we have employed a new approach using the supernatant and the sediment of centrifuged fluid gels to evaluate the different contributions.

The second objective of our study is to investigate the effects of co-solutes on fluid gel lubrication by using the proposed approach. In this work, glucose and glycerol were used to modify the solvent quality and the resulting changes in both particle structure and fluid gel properties were measured using tribology, rheology, texture analysis and light scattering techniques. Results show the substantial effect that both the continuous phase and particulate phase have on fluid gel lubrication. The observations from this study also suggest that controlling particle properties allows the lubrication properties to be manipulated, potentially enabling desirable sensory properties to be produced.

2. Materials and methods

2.1. Fluid gel production

Agar (A1296), D-glucose (G7021) and glycerol (49781) were purchased from Sigma Aldrich and used without further purification.

Agar was dispersed in distilled water at room temperature ($\approx 20^\circ\text{C}$) and then heated while stirring to 90°C until completely dissolved. The temperature was then lowered to approx. 70°C and co-solutes were dissolved into the hot solution.

Fluid gels were produced by pumping the hot solutions into a jacketed pin-stirrer device at a constant flow rate of 25 ml/min. The temperature of the cooling unit was kept at 15°C and the pin-stirrer was operated at a shear rate of 2000 rpm which is the maximum operation speed of the equipment.

Fluid gels with more than 30% glucose could not be produced reproducibly and thus data is not presented.

2.2. Tribology of fluid gels

The friction of the produced fluid gels was measured using a mini traction machine (MTM, PCS Instruments, London).

The tribometer was equipped with an elastomer disc (Samco Silicone Products) and a $\frac{3}{4}$ inch diameter AISI 400 stainless steel ball (PCS Instruments, London) as contact surfaces. These specific materials were selected since they have been previously shown to provide data with correlations to sensory perception ([Malone et al., 2003](#)). Fresh silicone discs were used for each test after cleaning by sonication for 5 min in ethanol followed by 5 min in distilled water. The stainless steel ball was cleaned with acetone and distilled water.

A normal load (W) of 2 N and a speed and slide-roll ratio (SRR) of 50% were used for all the experiments as they were found to yield the most reproducible data. Stribeck curves were generated by measuring the friction upon increasing the speed from $U = 1\text{--}1000$ mm/s followed by decreasing the speed from $U = 1000\text{--}1$ mm/s until a total of 6 runs were completed. Each test, consisting in 3 ramps up and 3 ramps down, was repeated 3 times. The error bars represent the 1 standard deviation of the mean of the 18 tests per fluid gel sample.

2.3. Particle size measurements

Particle size distribution was obtained using a Malvern Mastersizer 2000 with a water dispersion unit. A refractive index of 1.42 was used for the agar fluid gel particles, as previously reported by [Gabriele et al. \(2010\)](#).

2.4. Texture analysis

Compression test were performed on quiescently cooled agar gels using a TA.XT.plus Texture Analyser (Stable Micro Systems Ltd., UK) with a 40 mm diameter cylindrical aluminium probe. The height and diameter of the gel cylinders were 10 mm and 23 mm, respectively and the compression rate was 1 mm/s. The true stress σ_T and true strain ε_H were calculated using the following equations, as described elsewhere ([Moresi & Bruno, 2007](#); [Norton, Cox, & Spyropoulos, 2011](#)):

$$\sigma_E = F/A_0 \quad (1)$$

$$\varepsilon_E = (h - H_0)/H_0 \quad (2)$$

$$\varepsilon_H = \ln(1 + \varepsilon_E) \quad (3)$$

$$\sigma_T = \sigma_E(1 + \varepsilon_E) \quad (4)$$

where H_0 and A_0 are the initial height and cross-sectional area, h and F are the height and the compression force applied, ε_E and ε_H are the engineering and true (Henky) strain and σ_E and σ_T are the engineering and true stress.

2.5. Rheological tests

Dynamic oscillatory measurements were performed on a Kinexus Rheometer (Malvern Instruments Ltd., UK) using a cone and plate geometry (4° cone angle, 40 mm diameter).

Strain and stress sweep tests were carried out at 1 Hz on fluid gels 48 h after production.

3. Results and discussion

3.1. Effect of co-solutes on quiescent gels

Previously reported DSC studies on agar fluid gels produced using the method outlined in this paper showed that the enthalpy of melting of fluid gels is comparable to that of their quiescently cooled counterparts ([Norton et al., 1999](#)). This indicates that the intrinsic polymeric network and therefore the textural properties of the agar fluid gel particles are the same as those of the corresponding quiescent gels, as suggested by [Frith, Garijo, Foster, and Norton \(2002\)](#). Thus, in order to elucidate the effects of glycerol and glucose on gel particle stiffness, compression tests on quiescent gels were carried out.

Fig. 1A, 1B, 1C show the true stress-true strain profile for the quiescent gels produced with 1% [w/w] agar and increasing concentrations of glucose and glycerol. The changes in the textural properties of the gels were assessed in terms of the strain at failure and the Young's Modulus (E) which was obtained as the slope of the initial linear region of the curve (below 0.05 strain), as described in the work of Norton et al. (2011).

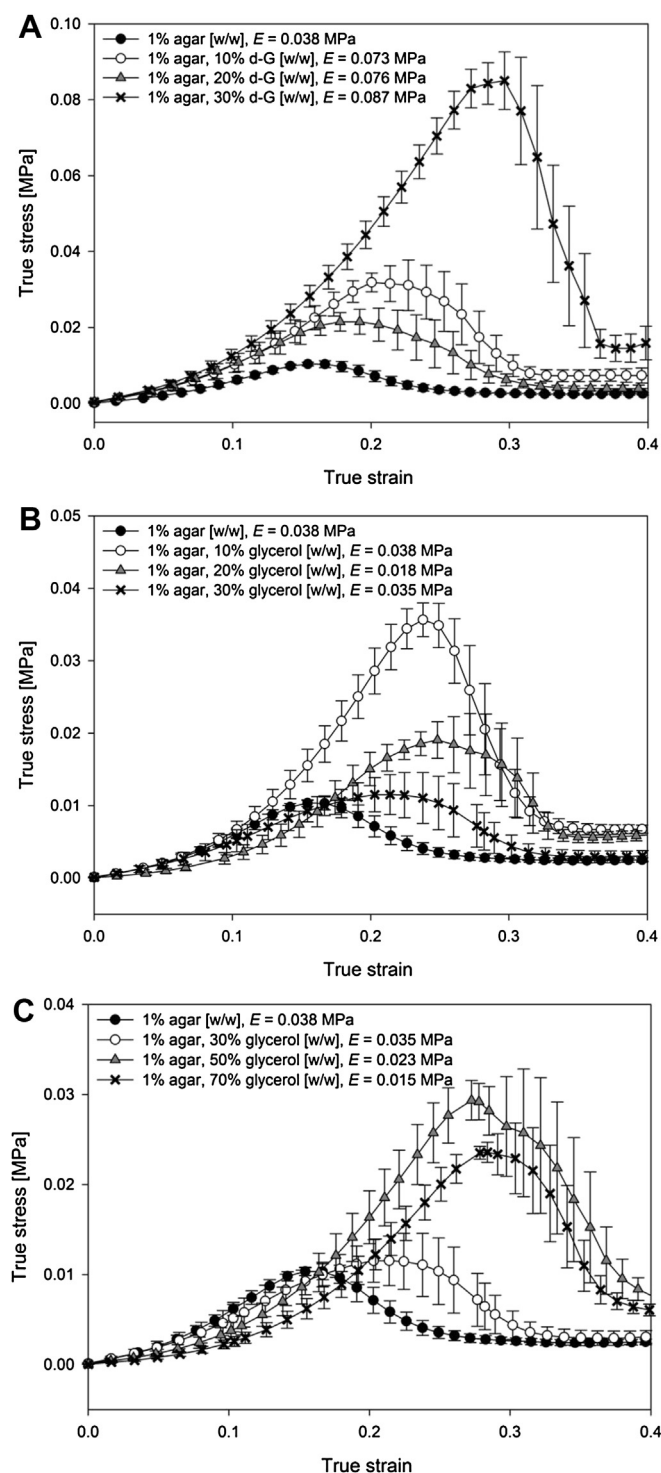


Fig. 1. A. True stress/true strain profiles for 1% [w/w] agar quiescent gel as function of glucose concentration. B. True stress/true strain profiles for 1% [w/w] agar quiescent gel as function of glycerol concentration. C. True stress/true strain profiles for 1% [w/w] agar quiescent gel as function of glycerol concentration.

The addition of glucose (up to 40%) leads to stiffer agar gels, as indicated by the gradual increase in E . The strain at failure also increases, indicating that gels become more deformable (less brittle) (Fig. 1A).

Although several studies have investigated the influence of sugars on the mechanical properties of polysaccharide gels, the underlying molecular mechanisms are still under debate in the literature. Small deformation tensile tests on agarose gels showed an increase in E with increasing the amount of added sucrose up to 15% (Nishinari et al., 1992). The authors used the model developed by Oakenfull and Scott (1986) to estimate the size of junction zones. From the rubber elasticity theory, Oakenfull and Scott (1986) derived the following equation relating the shear modulus (G) to the polymer concentration:

$$G = \frac{RTC}{M} \frac{M[J] - C}{M_J[J] - C} \quad (5)$$

Where M is the number average molecular weight of the polymer, M_J is the number average molecular weight of the junction zones, J is the number of junction zones, C is the weight concentration of polymer and R is the gas constant. The molar concentration of junction zones was calculated from $[J] = J/N_A$ where N_A is the Avogadro number. Assuming that G equals to 1/3 of E , theoretical plots of G versus agarose concentration as function of added sucrose were produced. Results indicated that the presence of sucrose leads to an increase in the number of junction zones but to the detriment of their size.

Watase, Nishinari, Williams, and Phillips (1990) reported an increase in E as well as an increase in both melting temperature (T_m) and the melting enthalpy (ΔH_m) with addition of either glucose or sucrose up to a critical sugar concentration, beyond which a reduction in the extent of ordering was measured. It was suggested that sugars, due to their hydroxyl groups, increase the hydrogen bonding thereby promoting both the formation and aggregation of helical domains. The helix structure of agarose is stabilised by hydrogen bonds with water, where some of the water molecules occupy the inner part of the helix (Foord & Atkins, 1989). Thus, a decrease in the extent of order (i.e. lower E and ΔH_m) is expected to occur at excessive sugar concentrations as the level of free water becomes insufficient to form thermodynamically stable junction zones.

The stabilisation of the agarose structure was later found to be dependent on the number of equatorially attached hydroxyl groups ($n(e\text{-OH})$) present in sugars, where an increase in E , T_m and setting temperature (T_s) was observed with increasing $n(e\text{-OH})$ (Watase, Kohyama, & Nishinari, 1992).

A zipper model approach to the gel-to-sol transition of thermo-reversible gels was proposed by Nishinari, Koide, Williams, and Phillips (1990). This approach describes the heat capacity of gels as function of the number of zipper (junction zones), the number of parallel links in a zipper, the rotational freedom of a parallel link and the energy enquired to open a link. Based on the zipper model approach, Watase et al. (1992) attributed the effect of increased E , T_m and T_s with increasing $n(e\text{-OH})$ to an increase in the number of junction zones and a reduction in both the size of each junction zone and the rotational freedom of a parallel link in a junction zone.

The suggestion of junction zones becoming smaller but more numerous provides an explanation for the increase in E at the intermediate level of glucose (up to 30%) measured in our work. However, the mechanism responsible for the increase in fracture strain at these glucose concentrations is not completely understood.

Similar to the results shown in our study, Normand et al. (2003) reported an increase in E as well as an increase in both the strain

and stress at failure with the addition of sucrose (up to 60%) to agarose gels. The turbidity and the wavelength exponent were shown to decrease with increasing added sucrose which was ascribed to a reduction in the degree of helix association, leading to finer (i.e. smaller cross-section radii) and greater number of bundles. This idea was supported by TEM micrographs which showed a more homogeneous network with smaller pore size for the agarose gels with added sucrose. The authors suggested that the increase in viscosity due to the presence of sucrose reduces the mobility of the polymer chains thereby limiting the aggregation of helices. An alternative explanation provided by Normand et al. (2003) was that sucrose increases the solvent quality such that the increased affinity of the agar helices for the solvent limits helix aggregation.

The effects of glucose on the textural properties of agar gels measured in our present work may be the result of the previously described mechanisms: 1. Formation of H-bonds between the OH groups present in both agar and sugars. 2. Change of the water structure. Both of these mechanisms are expected to take place simultaneously. However, the question remains as to which is dominant.

In this present work, a transition from a brittle to a deformable gel is also seen with an increasing level of glycerol (Fig. 1B, 1C). However, the evolution of E with the addition of glycerol differs from that of glucose. Addition of up to 10% glycerol has no effect on the E values. At glycerol concentrations above 10%, reduction in the E is observed with further increase in glycerol concentration. Glycerol is a polyol compound consisting of a 3-Carbon chain with 3 hydroxyl groups. As such, its ability to stabilise the agar gel structure is lower than glucose which, in solution, exists in equilibrium with several cyclic isomers containing equatorially attached hydroxyl groups.

The idea of reduced stabilisation by glycerol is supported by Watase et al. (1992) who found that, unlike glucose, addition of glycerol to agarose gels reduces both T_m and T_s . However, the height of the endothermic peak associated to the gel-to-sol transition was shown to increase with increasing concentrations of glycerol which led the authors to explain the reduced thermal stability in terms of an increased rotational freedom of the parallel links constituting a junction zone.

Overall, our results indicate an increase in both stiffness and deformability (as opposed to brittleness) with addition of glucose and a reduction in stiffness and increase in deformability with addition of glycerol.

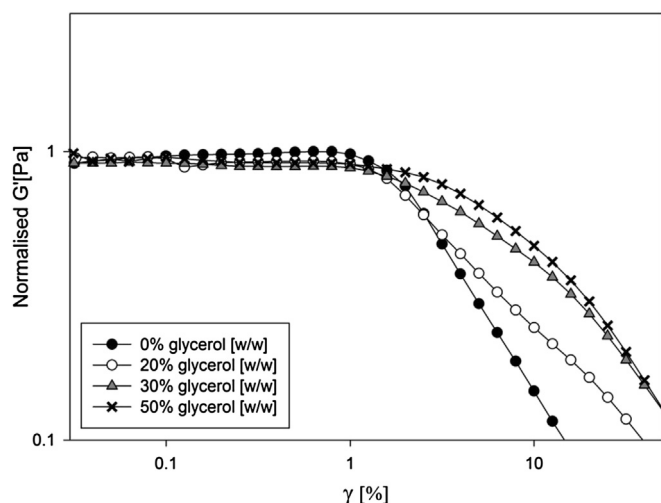


Fig. 2. Normalised elastic modulus vs complex strain of 1% agar FG (pin stirrer) mixed with glycerol.

3.2. Effect of co-solutes on fluid gels

The effects of glucose and glycerol on the structure of fluid gels have been investigated by small-strain dynamic oscillation measurements and light scattering experiments. Amplitude sweep tests were performed on the produced fluid gels and the obtained results are reported in Fig. 2, where a normalised G' is plotted as function of complex strain. Fluid gels produced with greater glycerol concentrations withstand larger strains before flowing which suggests increased particle deformability.

The particle stiffness and degree of inter-particle interaction were evaluated by stress sweep rheological measurements. The reduction in G' with increasing the level of glycerol (Fig. 3A) suggests that softer particles are produced. The yield stress, which can be inferred from the stress at which G' starts to decrease, also decreases with increasing glycerol content, indicating a lower degree of inter-particle interactions.

The decrease in particle stiffness with addition of glycerol is consistent with the reduction in E previously discussed for quiescent gels. It has been shown that the solubility of agar is higher in water than in a water-polyol mixture (Nishinari & Watase, 1987). The reduced degree of solvation of agar in a water-glycerol solvent is expected to change the ordering transition, possibly leading to faster rates of polymer aggregation. This would lead to larger, softer

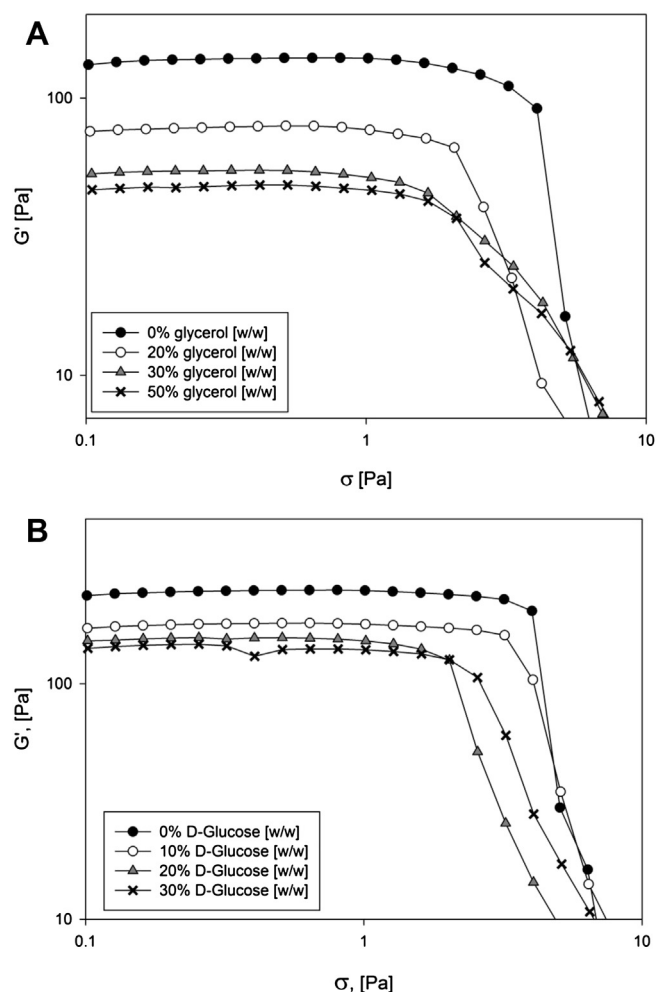


Fig. 3. A: Stress sweep at 1Hz for 1% agar fluid gels as function of glycerol concentration. B: Stress sweep at 1Hz for 1% agar fluid gels as function of glucose concentration.

and more deformable particles as the gelation process dominates over the applied shear rate in the kinetic competition during fluid gel formation.

Fluid gels exhibit a small progressive increase in gel particle size upon increasing the level of glycerol (Fig. 4A) which is in agreement with the idea of more rapid gelation and low shear impact.

Similar to glycerol, addition of glucose leads to fluid gels with reduced G' and reduced yield stress values (Fig. 3B). However, the reduction in G' is proportionally smaller for glucose than for glycerol. This decrease in G' does not correlate with the increase in E measured for quiescent gels with added glucose. Thus, the decrease in both G' and yield stress is attributed to a reduction in the degree of inter-particle interaction rather than changes to the physical properties of the particles with added glucose. This is supported by particle size distributions which show no discernable differences in particle size with increasing glucose concentration (Fig. 4B).

Agar is formed by a mixture of neutral agarose and negatively charged agaropectin. Thus, interactions between the weakly charged agar particles are expected to occur primarily due to van der Waal forces. An increased solvent quality for the agar polymer chains in solution with glucose would increase the affinity of the polymer for the solvent. This change of affinity may also impact upon the behaviour of the fluid gel particles in improved solvent quality.

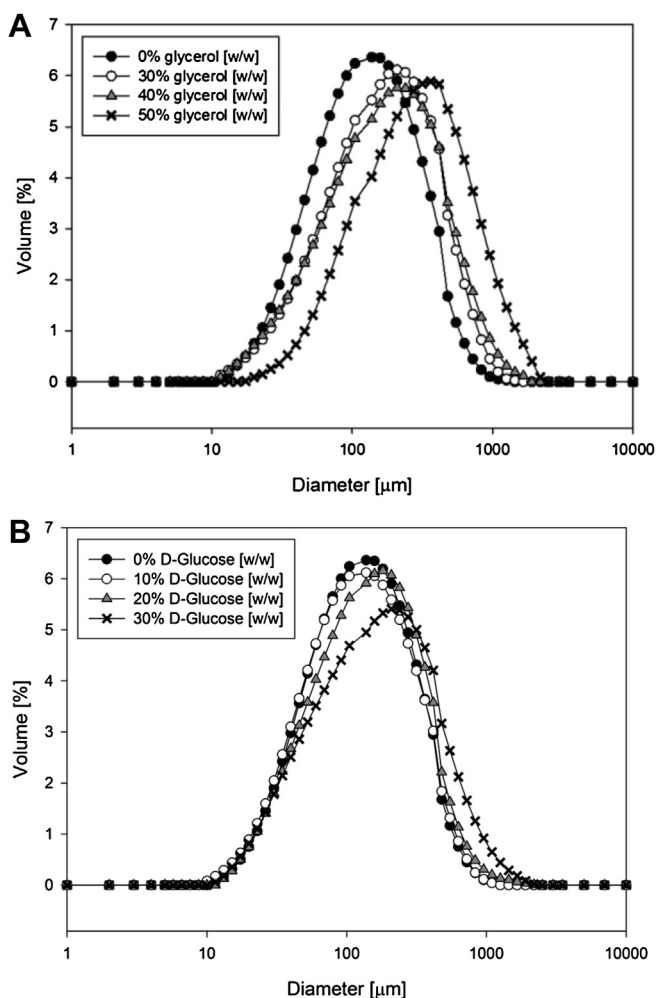


Fig. 4. A: Particle size distribution for 1% agar fluid gels as function of glycerol concentration. B: Particle size distribution of 1% agar fluid gels as function of glucose concentration.

The increased solvent quality for the fluid gels with added glucose is expected to reduce the level of the van der Waal forces acting between the particles.

In conclusion, the structural properties of fluid gel particles are not influenced by the addition of glucose. The presence of glycerol leads to a slight increase in particle size and a significant reduction in particle stiffness. The influence of the reduced stiffness of the particles on the lubricating properties of fluid gels will be discussed in Section 3.4.

3.3. Lubrication of agar fluid gels

Fig. 5 shows a comparison of the friction of water, the continuous phase, the gelled phase and fluid gels produced from 1% agar. The curve for fluid gels presents a behaviour that has been previously reported (Gabriele et al., 2010). That is, the friction decreases with increasing speed until reaching a critical speed in the mixed regime after which friction starts to increase until again decreasing at high speeds. A lubrication mechanism describing the three distinctive behaviours with increasing speed was suggested by Gabriele et al. (2010): At the starting condition, the ball and the disc are in dry contact with both particles and continuous phase excluded from the contact area. As the speed starts to increase, friction decreases due to the entrainment of the continuous phase. Particles remain excluded from the gap between the contacting surfaces as its size is smaller than the size of the particles (≈ 100 μm). Upon increasing the speed further, the gap widens until it reaches a size which is similar to the size of the particles, thereby allowing a monolayer of particles to enter the contact zone. This monolayer causes an increase in friction from the rolling-sliding motion of particles. At the highest speeds, multilayers of particles are entrained which further forces the two surfaces apart hence reducing friction again until reaching hydrodynamic regime where bulk fluid is entrained.

In this study, we have found that the friction of water is significantly higher than that of the fluid gels at all speeds. This finding suggests that the particles, rather than being excluded at low speeds, are entrained thereby providing lubrication by preventing contact between the two rotating surfaces.

It is possible that the ordering transition did not occur to its full extent during fluid gel production and thus some disordered polymer chains would remain dissolved in the continuous phase. The friction of the continuous phase containing the polymer would

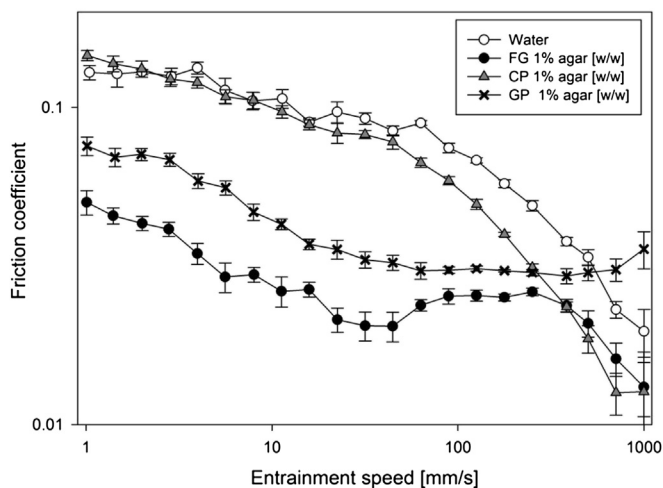


Fig. 5. Comparison of Stribeck curve for water, fluid gel (FG), continuous phase (CP), particulate gelled phase (GP) produced from 1% w/w agar.

then be expected to be lower than that of water as it entrains into the contact zone to form mixed fluid-boundary lubricating films, as previously reported (De Vicente, Stokes, & Spikes, 2006).

Thus, the question arises as to whether the entrainment of the continuous phase containing the polymer is the only mechanism responsible for the observed decrease in friction or, rather, both the continuous phase and the particulate gel particles are entrained in boundary and mixed regimes. In order to address this question, it becomes necessary to decouple the relevant contributions of the continuous phase and the gelled phase to fluid gel lubrication. To this end, fluid gels were centrifuged using a Sigma 3K30 centrifuge (Laborzentrifugen GmbH, Germany) at 120,000 rpm for 30 min at 20 °C and the resulting supernatant and the sediment were used as samples of the continuous phase and the particulate gelled phase, respectively. The continuous phase displays a behaviour similar to that of pure water at speeds up to 100 mm/s, above which the friction is lower than water, suggesting that a certain amount of disordered polymer chains are present in the continuous phase. The Stribeck curve of the continuous phase displays a trend which is expected for a non-absorbing hydrocolloid solution. The non-charged agar molecules do not adsorb onto the hydrophobic surface, thus effective boundary lubrication does not occur and the friction is similar to that of water. The friction is reduced below the value of water upon increasing the speed in the mixed regime due to the formation of an elastohydrodynamic film (De Vicente et al., 2006; Malone et al., 2003). Two mechanisms have been suggested for this reduction in friction (Malone et al., 2003): One mechanism is that the formation of the polymer layer prevents the two surfaces from contacting. The second mechanism is that the increased fluid viscosity suppresses turbulent flow in the contact area thus limiting drag.

That the friction of the continuous phase is equivalent to that of water at low speeds and significantly higher than that of the fluid gel confirms the idea of particle entrainment occurring at all speeds, which contradicts the model of fluid gel lubrication proposed by Gabriele et al. (2010). The suggestion of particles being present at the ball-in-disc gap at all speeds is also supported by previous data on fluid gels produced from agar (Gabriele et al., 2010), alginates (Fernández Farrés, Douaire, & Norton, 2013) and k-carrageenan (Garrec & Norton, 2013) which showed a reduction in friction on increasing the number and volume fraction of particles through raising polymer concentration.

At low rotational speeds in the mixed regime, the size of the film thickness is in the range of the size of the particles (microns). It is therefore likely that a film of microgel particles is confined within the gap at these speed conditions. This idea was first proposed by De Vicente et al. (2006) who showed that the friction of suspensions of neutralized carbopol microgelled particles (particle size of 2 μm –4 μm) was lower than that of water. The stribeck curve for these carbopol particles displayed a peak in the mixed regime but, unlike agar particles, friction did not decrease initially on increasing the speed from the stating conditions. Similar behaviour to that of these carbopol particles was reported for alginate fluids gels with particles having a size of 5 μm –10 μm (Fernández Farrés et al., 2013).

Thus, the difference in the lubricating behaviour at low speeds may relate to the physical properties of the confined particles. Agar particles, being reasonably large (100 μm), can deform into elongated shapes at low speeds in the tribometer where elongational flow is expected to dominate over shear flow. This results in a reduction of the contact area between the surfaces hence decreasing the measured friction. In contrast, the smaller alginate particles (Fernández Farrés et al., 2013), which are expected to be less deformable and harder than the agar particles, showed a peak in friction at the lowest speeds. The mechanism responsible for this peak in the Stribeck curve is at present not fully understood. It

could be consequence of the rolling and sliding motion of a particle monolayer, as previously suggested (Gabriele et al., 2010; de Wijk & Prinz, 2005). This is compatible with the idea of particle deformation occurring at the lowest speeds for the larger agar particle. As the speed is increased, the entrainment of the continuous phase would widen the gap until reaching the size of the individual

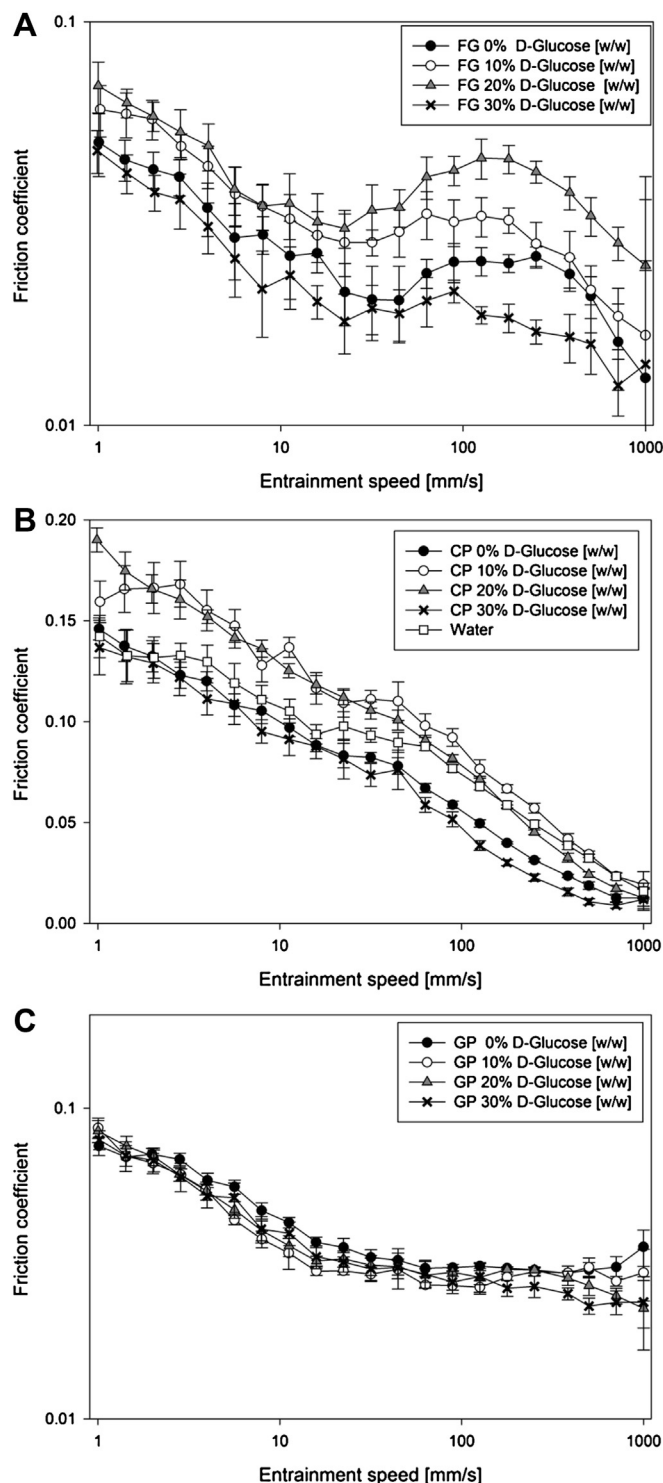


Fig. 6. A. Stribeck curves for 1% [w/w] agar fluid gels as function of glucose concentration. B. Stribeck curves for the aqueous continuous phase of 1% [w/w] agar fluid gels as function of glucose concentration. C. Stribeck curves for the particulate gelled phase of 1% [w/w] agar fluid gels as function of glucose concentration.

Table 1

Friction coefficient for aqueous solutions of glycerol and glucose. Data are the means of 3 Stribeck curves with standard deviations in parentheses.

	μ at 1 mm/s	μ at 125 mm/s	μ at 500 mm/s
Water	0.14 (0.02)	0.07 (0.003)	0.03 (0.004)
10% Glucose	0.12 (0.01)	0.04 (0.002)	0.02 (0.004)
10% Glycerol	0.15 (0.04)	0.05 (0.003)	0.02 (0.005)
20% Glucose	0.16 (0.03)	0.04 (0.002)	0.009 (0.004)
20% Glycerol	0.13 (0.03)	0.04 (0.003)	0.008 (0.004)
30% Glucose	0.14 (0.01)	0.05 (0.003)	0.01 (0.002)
30% Glycerol	0.13 (0.02)	0.05 (0.004)	0.009 (0.003)
50% Glycerol	0.13 (0.01)	0.04 (0.005)	0.01 (0.002)
70% Glycerol	0.12 (0.04)	0.02 (0.001)	0.005 (0.002)

particles. The rolling-sliding motion of these non-deformed particles as they enter the contact zone would increase friction. For the smaller particles, the rolling-sliding motion would occur at lower speeds, as the speed is increased from the static conditions.

Another possible explanation for the observed increase in friction is due to a build-up of particles around the ball-on-disc contact thus momentarily preventing the entrainment of the continuous phase. Although adsorption of the non-charged agar particles to the hydrophobic surface is not expected, a stick-slip motion of the confined particles could occur. This would increase the residence time of the confined particles at the contact zone, leading to accumulation of particles outside the inlet of the contact zone, building up around the ball-on-disc contact.

The results of our study have shown that the friction in both boundary and mixed regimes relates to the confinement of particles in the thin film. The friction in these two regimes is a function of the structure of the particles (e.g. size, elasticity). A determination the disordered polymer present in the continuous phase could be

achieved by spectroscopic techniques. This would further extend the developments presented in this work on the particulate phase and the continuous phase.

3.4. Lubrication of agar fluid gels with added co-solutes

The effects of glucose and glycerol on the lubrication properties of agar fluid gels have been investigated. As shown in Fig 6A, the lubrication by fluid gels is reduced at 10% and 20% glucose concentrations. Examining the lubrication provided by their corresponding continuous phase and gelled phase, it is seen that the decrease in lubrication of fluid gels with added glucose is caused by increased friction from the continuous phase (Fig 6B). The presence of glucose had no effect on the lubrication response of the gelled phase (Fig 6C) which is consistent with our previous suggestion that the structure of the particles remain unchanged for the range of glucose concentration studied.

The slight increase in the friction of the continuous phase is not attributed to changes in the water structure due to the presence of glucose since the differences between the friction of glucose solutions and that of water are negligible given the standard deviations (Table 1). The reason for the increase in friction of the continuous phase could be due to an increase in the hydrodynamic volume of the disordered free polymer chains at the inlet zone, reducing the entrainment of fluid to the contact area hence diminishing lubrication. This is expected to have an effect in the lubrication of agar which, due to its random coil conformation (Norton, Goodall, Austen, Morris, & Rees, 1986), is not expected to orient in the elongational and shear flow when compared to polysaccharides with rigid-rod or extended-coil conformations. As such, the ability of the disordered agar chains to provide lubrication by entering the

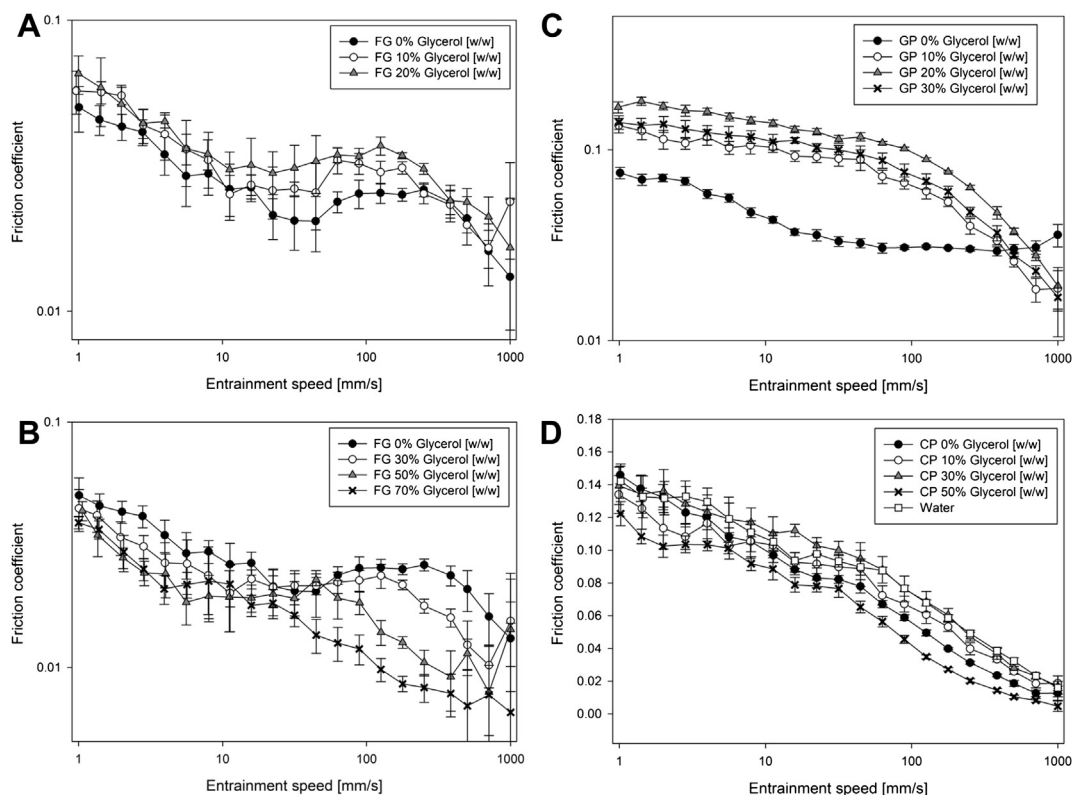


Fig. 7. A. Stribeck curves for 1% [w/w] agar fluid gels as function of glycerol concentration. B. Stribeck curves for 1% [w/w] agar fluid gels as function of glycerol concentration. C. Stribeck curves for the particulate gelled phase for 1% [w/w] agar fluid gels as function of glycerol concentration. D. Stribeck curves for the aqueous continuous phase of 1% [w/w] agar fluid gels as function of glycerol concentration.

contact zone in the presence of glucose may be diminished. More detail on the effect of hydrocolloid conformation on lubrication can be found in the work of Garrec and Norton (2012). The increase in the hydrodynamic volume of the disordered polymer chains could be the result of an increase in solvent quality at these low levels of glucose, as has been previously suggested (Normand et al. 2003; Sworn, & Kasapis, 1998).

At 30% concentration of glucose, the friction of fluid gels is similar to that of the fluid gels without added glucose due to the increased viscosity of the continuous phase overcoming the effect from the disordered polymer coils.

Examining the effects of glycerol, it is seen that the lubrication of fluid gels is reduced due to the increased friction of the particulate gel phase at low levels of glycerol (<30%) (Fig 7A–C). As showed earlier in this paper, fluid gel particles become larger and their stiffness decreases with increasing addition of glycerol. This reduction in particle stiffness can account for the higher friction coefficients. The ability of particles to support the applied load decreases as they become increasingly softer, leading to an increased contact area between the two rotating surfaces such that the sliding friction coefficient is increased. These observations are consistent with previous research on k-carrageenan fluid gels which showed a reduction in boundary friction by increasing particle stiffness (Garrec & Norton, 2013). Furthermore, larger particles typically yield higher friction coefficients, as reported elsewhere (de Wijk & Prinz, 2005).

Our previous hypothesis of gel particles being present at the contact area at all speeds is supported by the results presented in Fig. 7A which show that the increase in the friction of fluid gels due to the presence of softer particles occurs also at the lowest speeds.

Furthermore, the speed at which friction starts to increase is not affected by particle stiffness. This reinforces the view that particle entrainment takes place at all speeds as the speed required to induce particle entrainment is expected to depend on particle stiffness.

At glycerol concentrations above 30%, a shift in the lubrication mechanism is seen where friction progressively decreases with increasing glycerol concentration (Fig. 7B). At these levels of glycerol, the effect of increased friction due to particle deformability is suppressed with increased lubrication from the highly viscous continuous phase. The fluid gel tribology is now controlled by the continuous phase which forms a lubricating layer with a film thickness exceeding the size of the particles. The effect of increasing the continuous phase viscosity through raising glycerol concentration is to increase the film thickness such that lubrication is further enhanced. These observations suggest that, at a sufficiently high solvent viscosity, a thin-film lubrication mechanism prevails where the deformation and motion of the confined particles no longer determines friction. Overall, the use of glucose and glycerol as co-solutes for agar fluid gels has been shown to modify their lubricating behaviour by affecting both the particle structure and the continuous phase properties. Tribological measurements of the continuous and the gelled particulate phase have been used to evaluate their relative contribution to fluid gel lubrication while providing a further insight into the underlying mechanism.

3.5. Effect of applied normal load

In order to gain further insight into the mechanism responsible for the increase in friction in the mixed regime, a range of Stribeck curves were generated with increasing normal loads. For agar without added sugars, both the friction coefficient and the velocity at which friction starts to increase are not influenced by the applied normal load (Fig 8A). For agar fluid gels with added glycerol, the velocity associated with the peak in friction decreases slightly (Fig

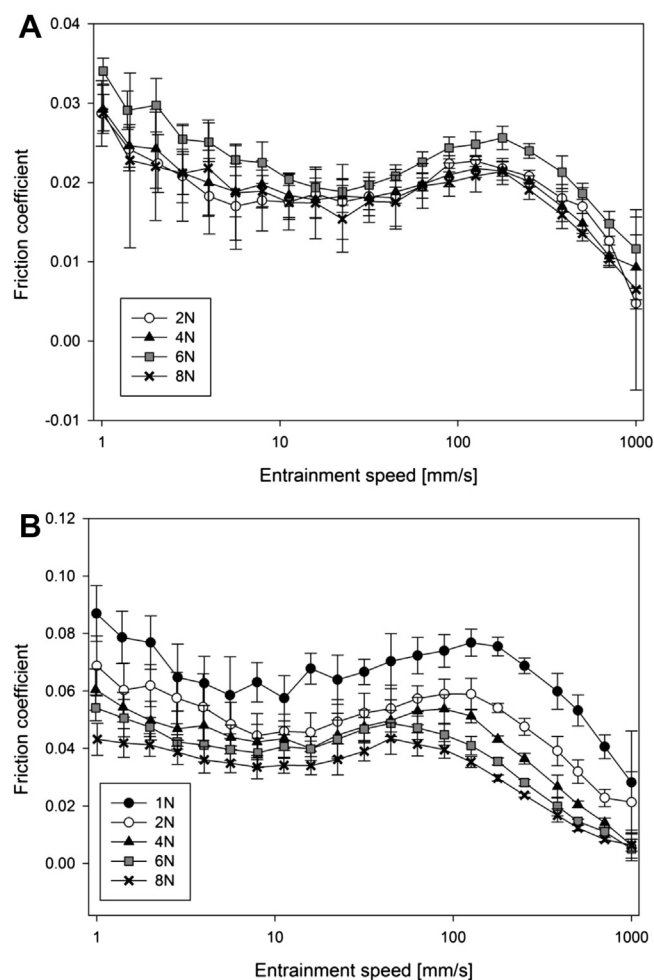


Fig. 8. A. Stribeck curves as function of applied normal load (W) for agar fluid gels. B. Stribeck curves as function of applied normal load (W) for agar fluid gels with added glycerol.

8B), which suggests a mechanism of particles building up around the ball-on-disc contact. On increasing the load, the width of the gap decreases leading to particles building up more rapidly around the contact for a given speed. The force exerted by the accumulated particles in front of the contact may then be greater at lower speeds for higher normal loads. However, the idea of particle accumulation must be considered as a tentative suggestion since fluid gels without added glycerol did not show this load dependence on friction. The reason for these two different behaviours is not yet clear but one possibility is that particle accumulation is promoted for the system with added glycerol due to the increased viscosity from the continuous phase. For these fluid gels with added glycerol, the friction coefficient decreases with increasing applied normal load which is expected for the compliant elastic surface used in this study, where the contact area is controlled by the elastic conformation over the plastic deformation at the contacting asperities.

According to the adhesion model (Bowden & Tabor, 1954), the contact between the surfaces takes place only between the asperity peaks and consequently, the real (interfacial) contact area A_r is lower than the apparent (geometrical) A_a contact area. During rolling-sliding, new contact points are constantly being created whilst others disassociate. On the assumption that A_r remains constant on average and the interfacial shear strength τ is the same for all asperity contacts, the tangential frictional force F_t is given by $F_t = \tau A_r$ (Bowden & Tabor, 1954).

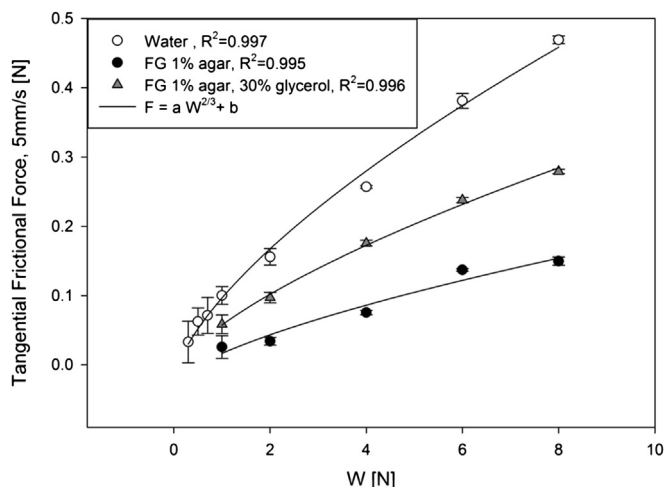


Fig. 9. Tangential Frictional force at 5 mm/s as function of applied normal load (W) for water, agar fluid gels and agar fluid gels with added glycerol.

From Hertz theory for elastic contacts, the contact area between elastically deforming asperities increases proportionally to $W^{2/3}$ (Hertz, 1881). Thus, assuming that the real contact area is proportional to the Hertzian contact area then $F_t \propto W^{2/3}$ is expected. The friction coefficient $\mu = F_t/W$ will then lead to $\mu \propto W^{2/3}/W \propto W^{-1/3}$.

Interestingly, whereas μ does not vary with W for fluid gels without glycerol, μ decreases with increasing W for fluid gels with glycerol. This behaviour is likely to be the consequence of the higher continuous phase viscosity of the system with added glycerol. In these systems, fluid film formation is enhanced due to the increased continuous phase viscosity which in turn increases the forces required to displace the continuous phase from the contact region. This enhanced lubrication from the continuous phase is expected to play a determining role on the effect of reduced μ with increasing W .

The deformability of the particles with glycerol could also be contributing to this observed behaviour, as more deformable particles would reduce the number of asperity contacts.

Plots of the tangential frictional force against the applied normal load are presented in Fig. 9 where data are fitted to $F_t \propto W^{2/3}$. Normal forces below 2 N led to large variability in the F_t data for fluid gels and so data could not be fitted to the equation. Over the range of data obtained, fluid gels show good agreement with theoretical predictions. The deviation between ideal Hertzian behaviour and that measured from these fluid gel systems may be due to variation from perfect slip conditions which is an underlying assumption in Hertz theory.

4. Conclusions

In this work, we have introduced a new approach to investigate the tribological behaviour of fluid gels using the continuous phase and the particulate gelled phase. Results showed that the friction of the continuous phase is higher than that of the fluid gel in boundary, mixed and hydrodynamic regime, indicating that the entrainment of particles takes place at all speeds, in disagreement with previous suggestions.

We have studied the structure and lubrication properties of agar fluid gels as function of solvent quality using a glucose and glycerol as co-solutes.

The addition of glucose (up to 30%) showed a minor effect on the structure of the particles and the particulate gelled phase displayed similar lubrication properties to the fluid gel with no added glucose. The friction of both the continuous phase and the fluid gels was

higher for the systems containing glucose. This was attributed to a greater hydrodynamic volume of the disordered polymer coils existing in the continuous phase due to the increased solvent quality upon adding glucose. The increase in the hydrodynamic volume of the agar random coils at the inlet zone limits the entrainment of the fluid to the contact area such that lubrication decreases.

The effect of glycerol is to increase particle size and reduce particle stiffness such that the ability of particles to support the applied load diminishes. As a result, the contact area between the surfaces increases thereby increasing friction. At high glycerol concentration, the lubrication of fluid gels is no longer driven by the presence of particles but it is governed by the continuous phase which forms a lubricating layer with a thickness exceeding the dimensions of the particles. As such, the friction gradually decreases as the viscosity of the continuous phase is increased by raising glycerol concentration. Experiments using Surface Force Apparatus technique (Israelachvili & McGuigan, 1990) where the interaction forces between the two contacting surfaces are measured would help to elucidate the exact processes involved during fluid gel lubrication.

Overall, results have shown that modifying both the kinetics of ordering transition and the degree of solvation of the hydrocolloid by changing solvent quality has a dramatic effect on the particle properties and thus the lubricating behaviour of fluid gels. The stiffness of the particles has a significant influence on lubrication as it determines the separation between the two tribological surfaces. Similarly, the continuous phase has an influence on fluid gel lubrication as it affects the film thickness as well as the structure of the disordered polymer coils.

As such, the lubrication properties of fluid gels cannot be predicted by rheology which is function of particle stiffness, particulate volume fraction as well as inter-particle interactions. This conclusion highlights the importance of studying the tribological properties together with rheology when designing food structures with desirable mouthfeel and textural attributes.

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References

- Araki, C. (1956). Structure of the agarose constituent of Agar-agar. *Bulletin of the Chemical Society of Japan*, 29(4), 543–544.
- Armisen, R., & Galatas, F. (2000). Agar. In G. O. Phillips, & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 21–40). Cambridge: Woodhead Publishing.
- Arnott, S., Fulmer, A. S. W. E., Scott, W. E., Dea, I. C. M., Moorhouse, R., & Rees, D. A. (1974). The agarose double helix and its function in agarose gel structure. *Journal of Molecular Biology*, 90(2), 269–284.
- Bowden, F. P., & Tabor, D. (1954). *The friction and lubrication of solids* (Vol. 1). Oxford Clarendon Press.
- De Vicente, J., Stokes, J. R., & Spikes, H. A. (2006). Soft lubrication of model hydrocolloids. *Food Hydrocolloids*, 20(4), 483–491.
- Fernández Farrés, I., Douaire, M., & Norton, I. T. (2013). Rheology and tribological properties of Ca-alginate fluid gels produced by diffusion-controlled method. *Food Hydrocolloids*, 32(1), 115–122.
- Foord, S. A., & Atkins, E. D. Y. (1989). New x-ray diffraction results from agarose: extended single helix structures and implications for gelation mechanism. *Biopolymers*, 28(8), 1345–1365.
- Frith, W. J., Garijo, X., Foster, T. J., & Norton, I. T. (2002). Microstructural origins of the rheology of fluid gels. *Special Publication-royal Society of Chemistry*, 278, 95–103.
- Gabriele, A., Spyropoulos, F., & Norton, I. T. (2010). A conceptual model for fluid gel lubrication. *Soft Matter*, 6(17), 4205–4213.
- Garrec, D. A., & Norton, I. T. (2012). The influence of hydrocolloid hydrodynamics on lubrication. *Food Hydrocolloids*, 26(2), 389–397.
- Garrec, D. A., & Norton, I. T. (2013). Kappa carrageenan fluid gel material properties. Part 2: Tribology. *Food Hydrocolloids*, 33(1), 160–167.
- Hertz, H. (1881). On the contact of elastic solids. *Journal für die reine und angewandte Mathematik*, 92, 156–171.

- Israelachvili, J. N., & McGuiggan, P. M. (1990). Adhesion and short-range forces between surfaces. Part I: new apparatus for surface force measurements. *Journal of Materials Research*, 5(10), 2223–2231.
- Malone, M. E., Appelqvist, I. A. M., & Norton, I. T. (2003). Oral behaviour of food hydrocolloids and emulsions. Part 1. Lubrication and deposition considerations. *Food Hydrocolloids*, 17(6), 763–773.
- Mills, T., Koay, A., & Norton, I. T. (2013). Fluid gel lubrication as a function of solvent quality. *Food Hydrocolloids*, 32(1), 172–177.
- Moresi, M., & Bruno, M. (2007). Characterisation of alginate gels using quasi-static and dynamic methods. *Journal of Food Engineering*, 82(3), 298–309.
- Morris, E. R. (1986). Molecular interactions in polysaccharide gelation. *British Polymer Journal*, 18(1), 14–21.
- Nishinari, K., Koide, S., Williams, P. A., & Phillips, G. O. (1990). A zipper model approach to the thermoreversible gel-sol transition. *Journal de Physique*, 51(16), 1759–1768.
- Nishinari, K., & Watase, M. (1987). Effects of polyhydric alcohols on thermal and rheological properties of polysaccharide gels (Food & Nutrition). *Agricultural and Biological Chemistry*, 51(12), 3231–3238.
- Nishinari, K., Watase, M., Kohyama, K., Nishinari, N., Oakenfull, D., Koide, S., et al. (1992). The effect of sucrose on the thermo-reversible gel-sol transition in agarose and gelatin. *Polymer Journal*, 24(9), 871–877.
- Normand, V., Aymard, P., Lootens, D. L., Amici, E., Plucknett, K. P., & Frith, W. J. (2003). Effect of sucrose on agarose gels mechanical behaviour. *Carbohydrate Polymers*, 54(1), 83–95.
- Norton, A. B., Cox, P. W., & Spyropoulos, F. (2011). Acid gelation of low acyl gellan gum relevant to self-structuring in the human stomach. *Food Hydrocolloids*, 25(5), 1105–1111.
- Norton, I. T., Frith, W. J., & Ablett, S. (2006). Fluid gels, mixed fluid gels and satiety. *Food Hydrocolloids*, 20(2), 229–239.
- Norton, I. T., Goodall, D. M., Austen, K. R. J., Morris, E. R., & Rees, D. A. (1986). Dynamics of molecular organization in agarose sulphate. *Biopolymers*, 25(6), 1009–1029.
- Norton, I. T., Jarvis, D. A., & Foster, T. J. (1999). A molecular model for the formation and properties of fluid gels. *International Journal of Biological Macromolecules*, 26(4), 255–261.
- Oakenfull, D., & Scott, A. (1986). Stabilization of gelatin gels by sugars and polyols. *Food Hydrocolloids*, 1(2), 163–175.
- Phillips, G. O., & Williams, P. A. (Eds.). (2009). *Handbook of hydrocolloids*. Elsevier.
- Schafer, S. E., & Stevens, E. S. (1995). A reexamination of the double-helix model for agarose gels using optical rotation. *Biopolymers*, 36(1), 103–108.
- Sworn, G., & Kasapis, S. (1998). Effect of conformation and molecular weight of co-solute on the mechanical properties of gellan gum gels. *Food Hydrocolloids*, 12(3), 283–290.
- Tako, M., & Nakamura, S. (1988). Gelation mechanism of agarose. *Carbohydrate Research*, 180(2), 277–284.
- Watase, M., Kohyama, K., & Nishinari, K. (1992). Effects of sugars and polyols on the gel-sol transition of agarose by differential scanning calorimetry. *Thermochimica Acta*, 206, 163–173.
- Watase, M., Nishinari, K., Williams, P. A., & Phillips, G. O. (1990). Agarose gels: effect of sucrose, glucose, urea, and guanidine hydrochloride on the rheological and thermal properties. *Journal of Agricultural and Food Chemistry*, 38(5), 1181–1187.
- de Wijk, R. A., & Prinz, J. F. (2005). The role of friction in perceived oral texture. *Food Quality and Preference*, 16(2), 121–129.